



## EUROPEAN PATENT APPLICATION

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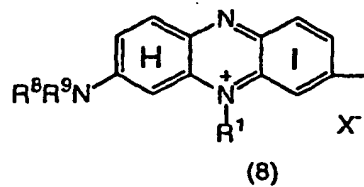
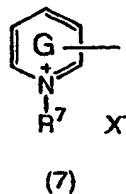
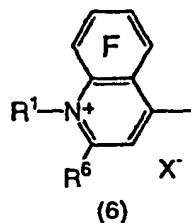
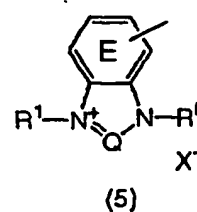
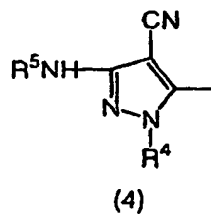
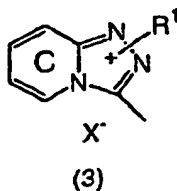
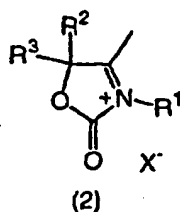
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## (54) Hair dye composition

(57) Provided is a hair dye composition containing a direct dye A-D=D-B. This hair dye composition has markedly high hair dyeing power, has less color fade over time and undergoes a small change in the color tone of the dye even after storage.

A represents any one of the following groups (2) to (8):



(in which R<sup>1</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup> each represents H, (substituted) C<sub>1-6</sub> alkyl group, etc., R<sup>2</sup> and R<sup>3</sup> each represents (substituted) C<sub>1-6</sub> alkyl group, etc., or form, when taken together with the adjacent C, a cycloalkane ring, Q represents N or group CR', R<sup>7</sup> represents (substituted) aralkyl group or a group CH<sub>2</sub>-CH(OH)-CH<sub>2</sub>-OR'', R<sup>8</sup> and R<sup>9</sup> each represents H, (substituted) C<sub>1-6</sub> alkyl, etc., or form, when taken together with the adjacent N, a heterocycle, X<sup>-</sup> represents an anion, and rings C-I may each have a further substituent or a condensed ring), D represents N or group CR''', and B represents

the residue of a coupling component.

## Description

### Technical Field

[0001] The present invention relates to a hair dye composition having markedly high dyeing power, can strongly impart the hair with an extremely vivid color ranging from yellow, red, purple to blue, has less color fade over time and undergoes a small change in the color tone of the dye even after storage.

### Background Art

[0002] Hair dyes can be classified by the dye to be used therefor, or whether they have bleaching action of melanin or not. Typical examples include a two-part permanent hair dye composed of a first part containing an alkali agent, an oxidation dye and a direct dye such as nitro dye and a second part containing an oxidizing agent; and one-part semi-permanent hair dye containing an organic acid or an alkali agent, and a direct dye such as acid dye, basic dye or nitro dye.

[0003] The above-described permanent hair dye is however accompanied with the drawbacks that color tone imparted by an oxidation dye is not so vivid and the color of the hair dyed with a vivid-color producing nitro dye ordinarily employed as a direct dye markedly fades over time and becomes dull soon even if the color tone rightly after dyeing is very vivid (Japanese Patent Application Laid-Open (*Kokai*) No. Hei 6-271435).

[0004] Recently, hair dyes containing as a direct dye a so-called cationic dye having a cation group contained in their conjugate system have been reported (Japanese Language Laid-Open Publication (PCT) No. Hei 8-507545, 8-501322 or 10-502946, or Japanese Patent Application Laid-Open (*Kokai*) No. Hei 10-194942). They have been found to involve drawbacks that intended dyeing effects are not available owing to decomposition of them caused by mixing, upon hair dyeing, with hydrogen peroxide ordinarily employed as an oxidizing agent; and that they are unstable to an alkali agent or a reducing agent essentially contained in a permanent hair dye.

### Disclosure of the Invention

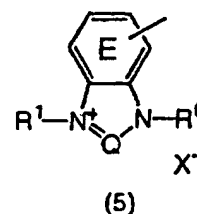
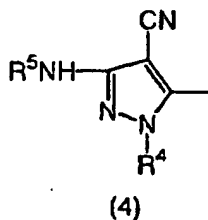
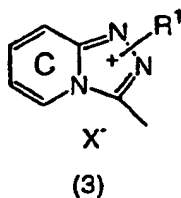
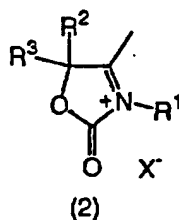
[0005] An object of the present invention is to provide a hair dye composition which has high hair dyeing power, less color fade over time, and excellent storage stability to permit only a small change in color tone of the dye after storage.

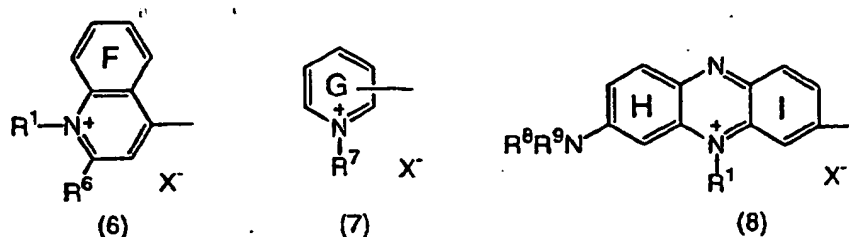
[0006] The present inventors have found that when the below-described compound which is known, as a dye for dyeing and printing therewith fiber materials, paper or leather, in *Offenlegungsschrift* DE-1569648, UK Patent Application GB 2054630, Japanese Patent Application Laid-Open (*Kokai*) Nos. Hei 7-224230, Sho 51-109024 and Sho 56-134280, *Offenlegungsschrift* DE 2347756, Japanese Patent Applications Laid-Open Nos. Sho 49-54685, Sho 49-54686 and Sho 49-54687, or as Basic Blue 16 and Basic Black 2 is used as a hair dye, the resulting dye composition can strongly impart the hair with a vivid color ranging from yellow, red, purple to blue without decomposing the dye upon hair dyeing, exhibits excellent light resistance, washing resistance, perspiration resistance, friction resistance and heat resistance, and undergoes a small change in the color tone of the dye after storage as compared with that rightly after preparation because the dye exists in the composition stably.

[0007] In one aspect of the present invention, there is thus provided a hair dye composition comprising, as a direct dye, a compound represented by the following formula (1):



wherein, A represents a group of the following formula (2), (3), (4), (5), (6), (7) or (8):





(in which, R<sup>1</sup> and R<sup>6</sup> each independently represents a C<sub>1-6</sub> alkyl group which may have a substituent, an alkenyl group which may have a substituent or an aryl group which may have a substituent, R<sup>2</sup> and R<sup>3</sup> each independently represents a C<sub>1-6</sub> alkyl group which may have a substituent, an alkenyl group which may have a substituent, an aryl group which may have a substituent, or R<sup>2</sup> and R<sup>3</sup>, when taken together with the adjacent carbon atom, form a 5- to 7-membered cycloalkane ring, R<sup>4</sup> represents a hydrogen atom, a C<sub>1-6</sub> alkyl group which may have a substituent, an alkenyl group which may have a substituent, or an aryl group which may have a substituent, R<sup>5</sup> represents a hydrogen atom, a C<sub>1-6</sub> alkyl group which may have a substituent, an alkenyl group which may have a substituent, an aryl group which may have a substituent, an acyl group, an alkoxycarbonyl group, a carbamoyl group, an alkylsulfonyl group or an arylsulfonyl group, Q represents a nitrogen atom or a group CR' (in which R' represents a hydrogen atom, a C<sub>1-6</sub> alkyl group which may have a substituent, an alkenyl group which may have a substituent or an aryl group which may have a substituent), R<sup>7</sup> represents an aralkyl group which may have a substituent or a group CH<sub>2</sub>-CH(OH)-CH<sub>2</sub>-OR" (in which R" represents a C<sub>1-6</sub> alkyl group which may have a substituent, an alkenyl group which may have a substituent or an aryl group which may have a substituent), R<sup>8</sup> and R<sup>9</sup> each independently represents a hydrogen atom, a C<sub>1-6</sub> alkyl group which may have a substituent, an alkenyl group which may have a substituent or an aryl group which may have a substituent, or R<sup>8</sup> and R<sup>9</sup>, when taken together with the adjacent nitrogen atom, form a nitrogen-containing heterocycle, X<sup>-</sup> represents an anion, and rings C, E, F, G, H and I may each independently have a further substituent or may be cyclocondensed with another aromatic ring),

D represents a nitrogen atom or a group CR'" (in which P'" represents a hydrogen atom or a C<sub>1-6</sub> alkyl group which may have a substituent), and

B represents the residue of a phenol, aniline, acylacetooarylamide, pyridone, quinoline, isoquinoline, pyrazole, indole, diphenylamine, aminopyridine, pyrimidine, pyrimidone, naphthol, naphthylamine, aminothiazole, thiophene or hydroxypyridine type coupling component.

[0008] In another aspect of the present invention, there is also provided a method for dyeing the hair with the above-described hair dye composition.

### Best Mode for Carrying out the Invention

[0009] Examples of the C<sub>1-6</sub> alkyl group represented by R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>8</sup>, R<sup>9</sup>, R', R" or R'" include methyl, ethyl, propyl, isopropyl and cyclohexyl groups; those of the alkenyl group include vinyl, allyl and isobutenyl groups; and those of the aryl group include phenyl and naphthyl groups, each of which may be substituted by an aryl group, cyano group, halogen atom, hydroxyl group, C<sub>1-4</sub> alkoxy group, C<sub>1-4</sub> hydroxyalkoxy group, alkoxycarbonyl group, heterocyclic group, group NR<sup>10</sup>R<sup>11</sup> (in which R<sup>10</sup> and R<sup>11</sup> each independently represents a hydrogen atom, a C<sub>1-6</sub> alkyl group which may have a substituent or an aryl group which may have a substituent).

[0010] Examples of the cycloalkane ring formed by R<sup>2</sup> and R<sup>3</sup> when they are taken together with the adjacent carbon atom include cyclopentane, cyclohexane and cycloheptane rings.

[0011] Examples of the acyl group represented by R<sup>5</sup> include formyl, acetyl and propionyl groups, those of the alkoxycarbonyl group include methoxycarbonyl and ethoxycarbonyl groups; those of the alkylsulfonyl group include methanesulfonyl group; and those of the arylsulfonyl group include benzenesulfonyl and toluenesulfonyl groups.

[0012] Examples of the aralkyl group represented by R<sup>7</sup> include benzyl and phenethyl groups.

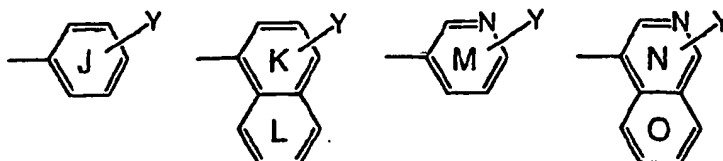
[0013] Examples of the nitrogen-containing heterocycle formed by R<sup>8</sup> and R<sup>9</sup> when they are taken together with the adjacent nitrogen atom include pyrrolidine, piperidine, morpholine and piperazine rings, each of which may be substituted by an alkyl group.

[0014] Examples of the substituent which an aralkyl group represented by R<sup>7</sup> or the ring C, E, F, G or H may have include alkyl groups, aryl groups, alkoxy groups, amino group, mono- or di-alkylamino groups, hydroxy group, cyano group, nitro group, acylamino groups, halogen atoms and alkoxycarbonyloxy groups, more specifically, methyl, ethyl, methoxy, ethoxy, chlorine and bromine. As another aromatic ring with which the above-described ring may be cyclocondensed

condensed, the benzene ring may be given as an example.

[0015] Examples of the anion represented by  $X^-$  include chloride ions, bromide ions, iodide ions, trichlorozincic acid ions, tetrachlorozincic acid ions, sulfuric acid ions, hydrosulfuric acid ions, methyl sulfate ions, phosphoric acid ions, formic acid ions and acetic acid ions.

[0016] Examples of the residue of a coupling component represented by B include those represented by the following formulas:

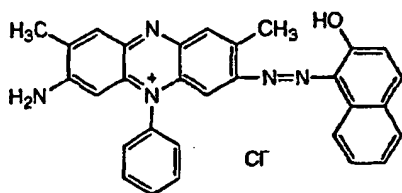


wherein, Y represents a hydroxy group or a group  $-NR^{12}R^{13}$  (in which  $R^{12}$  and  $R^{13}$  each independently represents a hydrogen atom, a  $C_{1-6}$  alkyl group which may have a substituent, an alkenyl group which may have a substituent or an aryl group which may have a substituent, or  $R^{12}$  and  $R^{13}$ , when taken together with the adjacent nitrogen atom, form a nitrogen-containing heterocycle), and rings J, K, L, M, N and O may each have a further substituent.

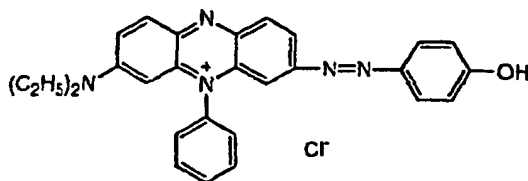
[0017] As the alkyl, alkenyl and aryl groups represented by  $R^{12}$  or  $R^{13}$ , and substituents therefor, nitrogen-containing heterocyclic group formed by them, and substituents for the rings J to O, those similar in the above-described group A can be given as examples.

[0018] Specific examples of the direct dye (1) to be used in the present invention will next be shown.

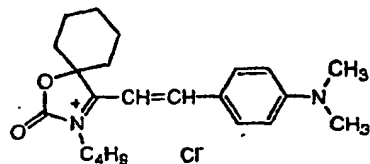
Compound (a)



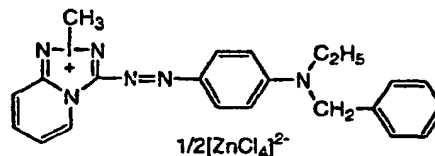
Compound (b)



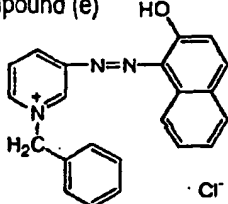
Compound (c)



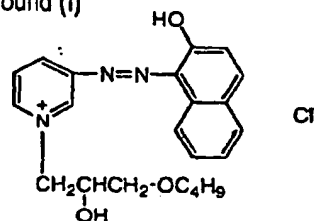
Compound (d)



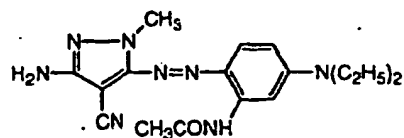
Compound (e)



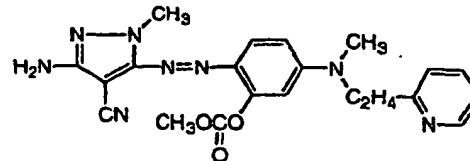
Compound (f)



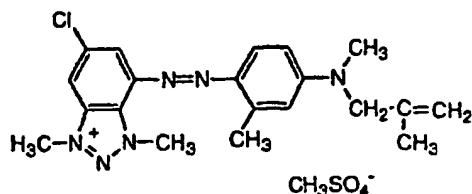
Compound (g)



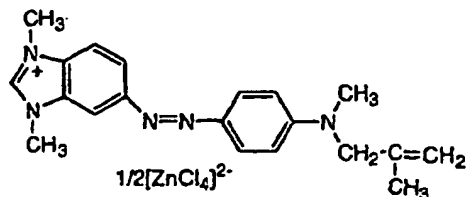
Compound (h)



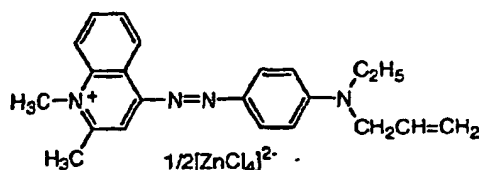
Compound (i)



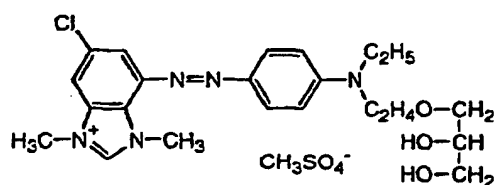
Compound (j)



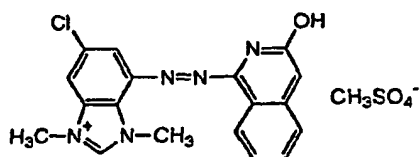
Compound (k)



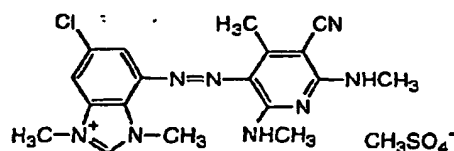
Compound (l)



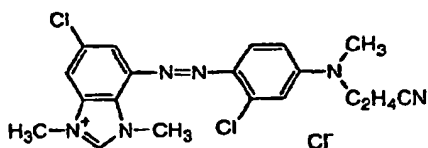
Compound (m)



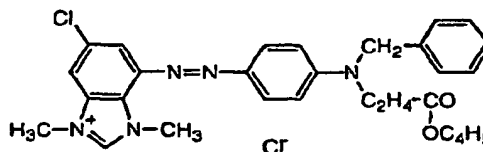
Compound (n)



Compound (o)



Compound (p)



[0019] As a direct dye, at least one of these direct dyes (1) can be used or another direct dye can be used in combination therewith. In particular, when the direct dye (1) is a yellow dye, combination with red and blue dyes, when the direct dye is a red dye, combination with yellow and blue dyes, and when the direct dye (1) is a blue dye, combination with yellow and red dyes each makes it possible to dye the hair with a deep and highly lustrous dark brown or black color.

[0020] Examples of the direct dye other than the direct dyes (1) include Basic Blue 7 (C.I. 42595), Basic Blue 26 (C.I. 44045), Basic Blue 99 (C.I. 56059), Basic Violet 10 (C.I. 45170), Basic Violet 14 (C.I. 42515), Basic Brown 16 (C.I. 12250), Basic Brown 17 (C.I. 12251), Basic Red 2 (C.I. 50240), Basic Red 22 (C.I. 11055), Basic Red 76 (C.I. 12245), Basic Red 118 (C.I. 12251:1) and Basic Yellow 57 (C.I. 12719); and basic dyes as described in Japanese Patent

[0021] The direct dye (1) is preferably added in an amount of 0.01 to 20 wt.%, more preferably 0.05 to 10 wt.%, especially 0.1 to 5 wt.% based on the whole composition (after mixture of all the component parts when the hair dye composition is a two part or three part type; this will apply equally hereinafter). When another direct dye is added in combination, the content of it in total with the direct dye (1) preferably ranges from 0.05 to 10 wt.%, especially 0.1 to 5 wt.%.

[0022] The hair dye composition of the present invention is preferably adjusted to pH 6 to 11, with pH 8 to 11 being especially preferred. Examples of the alkali agent to be used for pH adjustment include ordinarily employed ones such as ammonia, organic amines and salts thereof. The alkali agent is preferably added in an amount of 0.01 to 20 wt.%, more preferably 0.1 to 10 wt.%, especially 0.5 to 5 wt.% based on the whole composition.

[0023] In the hair dye composition of the present invention, an oxidizing agent can be incorporated. In this case, hair dyeing and bleaching can be carried out simultaneously, which facilitates more vivid hair dyeing. Ordinarily employed oxidizing agents, for example, hydrogen peroxide, persulfates such as ammonium persulfate, potassium persulfate and sodium persulfate, perborates such as sodium perborate, percarbonates such as sodium percarbonate and bromates such as sodium bromate and potassium bromate are usable. Out of them, hydrogen peroxide is especially preferred. The oxidizing agent is preferably added in an amount of 0.5 to 10 wt.%, especially 1 to 8 wt.%, based on the whole composition.

[0024] In the hair dye composition of the present invention, an oxidation dye can be incorporated further. This incorporation enables markedly vivid dyeing not attainable by the single use of an oxidation dye. In this case, the above-exemplified oxidizing agents can be used as an oxidizing agent, with hydrogen peroxide being particularly preferred. Alternatively, an oxidizing enzyme such as laccase can be employed. For the oxidation dye, known color developers and couplers ordinarily employed for an oxidation type hair dye can be used.

[0025] Examples of the developer include p-phenylenediamines having one or several groups selected from groups  $\text{NH}_2$ -,  $\text{NHR}$ - and  $\text{NR}_2$ - (in which R represents a  $\text{C}_{1-4}$  alkyl group or a hydroxyalkyl group) such as p-phenylenediamine, p-toluylenediamine, N-methyl-p-phenylenediamine, chloro-p-phenylenediamine, 2-(2'-hydroxyethylamino)-5-aminotoluene, N,N-bis-(2-hydroxyethyl)-p-phenylenediamine, 2-hydroxyethyl-p-phenylenediamine, 2,6-dimethyl-p-phenylenediamine, methoxy-p-phenylenediamine, 2,6-dichloro-p-phenylenediamine, 2-chloro-6-methyl-p-phenylenediamine, 6-methoxy-3-methyl-p-phenylenediamine, 2,5-diaminoanisole, N-(2-hydroxypropyl)-p-phenylenediamine and N-2-methoxyethyl-p-phenylenediamine; 2,5-diaminopyridine derivatives and 4,5-diaminopyrazole derivatives; p-aminophenols such as p-aminophenol, 2-methyl-4-aminophenol, N-methyl-p-aminophenol, 3-methyl-4-aminophenol, 2,6-dimethyl-4-aminophenol, 3,5-dimethyl-4-aminophenol, 2,3-dimethyl-4-aminophenol and 2,5-dimethyl-4-aminophenol; o-aminophenols, o-phenylenediamines, 4,4'-diaminophenylamine and hydroxypropylbis(N-hydroxyethyl-p-phenylenediamine); and salts thereof.

[0026] Examples of the coupler include 1-naphthol, 1,5-dihydroxynaphthalene, 1,7-dihydroxynaphthalene, 2,7-dihydroxynaphthalene, 5-amino-2-methylphenol, 5-(2'-hydroxyethylamino)-2-methylphenol, 2,4-diaminoanisole, m-toluylenediamine, resorcin, m-phenylenediamine, m-aminophenol, 4-chlororesorcin, 2-methylresorcin, 2,4-diaminophenoxyethanol, 2,6-diaminopyridine, 2-amino-3-hydroxypyridine, 4-hydroxyindole, 6-hydroxyindole, 2,4-diamino-6-hydroxypyrimidine, 2,4,6-triaminopyrimidine, 2-amino-4,6-dihydroxypyrimidine, 4-amino-2,6-dihydroxypyrimidine, 4,6-diamino-2-hydroxypyrimidine and 1,3-bis(2,4-diaminophenoxy)propane; and salts thereof.

[0027] As each of a developer and a coupler, at least one of the above-exemplified ones can be used. Each of them is preferably added in an amount of 0.01 to 20 wt.%, especially 0.5 to 10 wt.% based on the whole composition.

[0028] To the hair dye composition of the present invention, a known autooxidation dye typified by an indole or an indoline, or a known direct dye such as a nitro dye or a disperse dye can also be added.

[0029] When an anionic component (such as anionic surfactant or anionic polymer) is added to the hair dye composition of the present invention in the case where the direct dye (1) is cationic, it is preferred to satisfy the following equation:

$$\text{"Ion activity concentration of the anionic component/ion activity concentration of the cationic direct dye (1)} \leq 8"$$

The term "ion activity concentration" as used herein means "molar concentration x ionic valence".

[0030] Addition of a polyol, polyol alkyl ether, cationic or amphoteric polymer or silicone to the hair dye composition of the present invention is preferred, because the resulting composition can dye the hair uniformly and has improved cosmetic effects of the hair.

[0031] In addition to the above-described components, those ordinarily employed as a raw material for cosmetics can be added to the hair dye composition of the present invention. Examples of such an optional component include hydrocarbons, animal or vegetable fats and oils, higher fatty acids, organic solvents, penetration promoters, cationic surfactants, natural or synthetic polymers, higher alcohols, ethers, amphoteric surfactants, nonionic surfactants, protein

derivatives, amino acids, antiseptics, chelating agents, stabilizing agents, antioxidants, plant extracts, crude drug extracts, vitamins, colorants, perfumes and ultraviolet absorbers.

[0032] The hair dye composition of the present invention can be prepared in a conventional manner into a one-part composition, a two-part composition having a first component part containing an alkali agent and a second component part containing an oxidizing agent, or a three-part composition having, in addition to these two component parts, a powdery oxidizing agent such as persulfate. The direct dye (1) can be incorporated in either one or both of these component parts of the two-part or three-part composition. When the hair dye composition of the present invention is one-part type, it is applied to the hair directly, while the two- or three-part type is applied to the hair after mixing these parts upon hair dyeing.

[0033] No particular limitation is imposed on the form of the hair dye composition of the present invention. Examples include powder, transparent liquid, emulsion, cream, gel, paste, aerosol, and aerosol foam. It preferably has a viscosity of 2000 to 100000 mPa-s in the stage of application to the hair (after mixing of all the components when the hair dye composition is a two-part or three-part type).

#### -Examples-

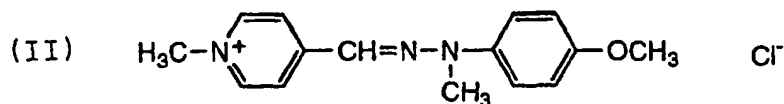
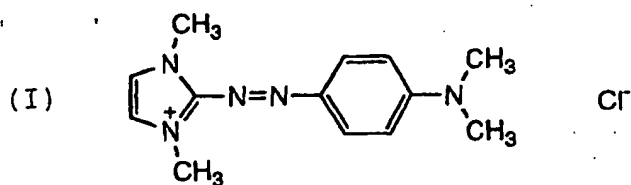
##### Examples 1 to 5

[0034] In a manner known per se in the art, hair dyes as shown in Table 1 were prepared.

Table 1

(wt.%)	Examples				
	1	2	3	4	5
Dye [Compound (a)]	0.2		0.15	0.1	0.2
Dye [Compound (b)]		0.5		0.1	
Dye [Compound (c)]		0.3		0.1	0.2
Dye [formula (I), Red]			0.15		0.05
Dye [formula (II), Yellow]			0.1	0.1	
Ethanol		5		5	5
Propylene glycol			5		5
Diethylene glycol monoethyl ether		10			
Guar gum	1				
Hydroxypropyl guar gum		1	1	1	1
"Gutquat 734" (trade name; product of ISP Japan)	1		1		
"Catinal LC100" (trade name; product of Toho Chemical Industry)		1			1
"Polyether-modified silicone KF6005" (trade name; product of Shin-Etsu Chemical)					0.4
"Amodimethicone SM8702C" (trade name; product of Dow Coming Toray Silicone)				1.5	
Monoethanolamine	0.1				
Phosphoric acid	Amount to adjust pH to 9				
Perfume	q.s.				
Water	Balance				





Examples 6 to 9

[0035] In a manner known per se in the art, hair dyes as shown in Table 2 were prepared.

Table 2

(wt.%) (wt%)		Examples			
		6	7	8	9
1st part	Dye [Compound (a)]	0.2		0.15	0.2
	Dye [Compound (d)]		0.1	0.15	
	Dye [Compound (e)]		0.1	0.15	
	Dye [formula (I), Red]		0.1		0.05
	28 wt.% Aqueous ammonia	5			
	Monoethanolamine	2			
	Propylene glycol	8			
	Polyoxyethylene (20) isostearyl ether	24			
	Polyoxyethylene (2) isostearyl ether	20			
	"Merquat 280" (trade name; product of Calgon Corp., a 35 wt.% aqueous solution)	8			
	"Polymer JR400" (trade name; product of Union Carbide)		0.5		0.5
	"Amodimethicone SM8702C" (trade name; product of Dow Corning Toray Silicone)			2	
	"Polyether modified silicone KF6005" (trade name; product of Shin-Etsu Chemical)				0.3
	Tetrasodium ethylenediaminetetraacetate	0.1			
	Perfume	q.s.			
	Ammonium chloride	Amount to adjust pH to 10			
	Water	Balance			
2nd part	35 wt.% Aqueous hydrogen peroxide	17.1			
	Methylparaben	0.1			
	Phosphoric acid	Amount to adjust pH to 3.5			
	Water	Balance			

[0036] In a manner known per se in the art, hair dyes as shown in Table 3 were prepared.

Table 3

(wt.%)		Examples		
		10	11	12
1st part	Toluene-2,5-diamine	1.9	1	
	Para-aminophenol			1
	Resorcin	2		
	Para-amino-ortho-cresol			1.1
	2,4-Diaminophenoxyethanol		1.37	
	Dye [Compound (f)]	0.05		
	Dye [Compound (g)]		0.15	
	Dye [Compound (k)]			0.1
	28 wt.% Aqueous ammonia	5		
	Monoethanolamine	2		
	Propylene glycol	8		
	Polyoxyethylene (20) isostearyl ether	24		
	Polyoxyethylene (2) isostearyl ether	20		
	"Merquat 280" (trade name; product of Calgon Corp., a 35 wt.% aqueous solution)	8		
	"Polymer JR400" (trade name; product of Union Carbide)		0.5	
	"Amodimethicone SM8702C" (trade name; product of Dow Coming Toray Silicone)			2
	Sodium sulfite	0.05		
	Ascorbic acid	0.5		
	Tetrasodium ethylenediaminetetraacetate	0.1		
	Perfume	q.s.		
2nd Part	Ammonium chloride	Amount to adjust pH to 10		
	Water	Balance		
	35 wt.% Aqueous hydrogen peroxide	17.1		
	Methylparaben	0.1		
	Phosphoric acid	Amount to adjust pH to 3.5		
	Water	Balance		

Examples 13 & 14

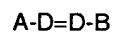
[0037] In a manner known per se in the art, the following hair dye was prepared.

Table 4

(wt.%)		Examples	
		13	14
1st part part	Para-aminophenol	1	
	Para-amino-ortho-cresol	1.1	
	Compound (a)	0.1	
	Compound (n)		0.1
	28 wt.% Aqueous ammonia	5	
	Monoethanolamine	2	
	Cetanol	8.5	
	Polyoxyethylene (40) cetyl ether	3	
	Polyoxyethylene (2) cetyl ether	3.5	
	Stearyl trimethyl ammonium chloride	2	
	Liquid paraffin	0.5	
	Sodium sulfite	0.05	
	Ascorbic acid	0.5	
	Tetrasodium ethylenediaminetetraacetate	0.1	
	Perfume	q.s.	
	Ammonium chloride	Amount to adjust pH to 10	
	Water	Balance	
2nd part	35 wt.% Aqueous hydrogen peroxide	17.1	
	Methylparaben	0.1	
	Phosphoric acid	Amount to adjust pH to 3.5	
	Water	Balance	

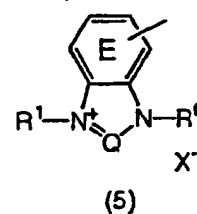
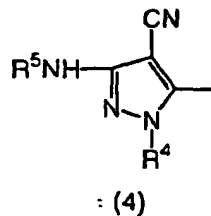
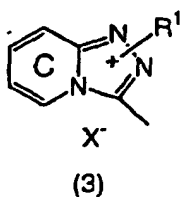
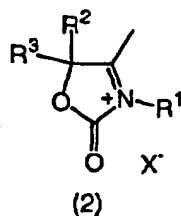
### Claims

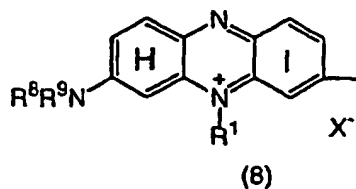
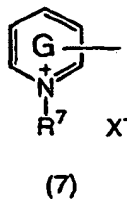
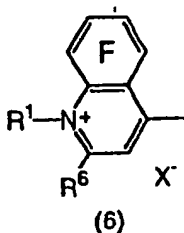
1. A hair dye composition comprising, as a direct dye, a compound represented by the following formula (1):



(1)

wherein, A represents a group of the following formula (2), (3), (4), (5), (6), (7) or (8):





(in which, R<sup>1</sup> and R<sup>6</sup> each independently represents a C<sub>1-6</sub> alkyl group which may have a substituent, an alkenyl group which may have a substituent or an aryl group which may have a substituent, R<sup>2</sup> and R<sup>3</sup> each independently represents a C<sub>1-6</sub> alkyl group which may have a substituent, an alkenyl group which may have a substituent, an aryl group which may have a substituent, R<sup>2</sup> and R<sup>3</sup> form, when taken together with the adjacent carbon atom, a 5- to 7-membered cycloalkane ring, R<sup>4</sup> represents a hydrogen atom, a C<sub>1-6</sub> alkyl group which may have a substituent, an alkenyl group which may have a substituent, or an aryl group which may have a substituent, R<sup>5</sup> represents a hydrogen atom, a C<sub>1-6</sub> alkyl group which may have a substituent, an alkenyl group which may have a substituent, an aryl group which may have a substituent, an acyl group, an alkoxycarbonyl group, a carbamoyl group, an alkylsulfonyl group or an arylsulfonyl group, Q represents a nitrogen atom or a group CR' (in which R' represents a hydrogen atom, a C<sub>1-6</sub> alkyl group which may have a substituent, an alkenyl group which may have a substituent or an aryl group which may have a substituent), R<sup>7</sup> represents an aralkyl group which may have a substituent or a group CH<sub>2</sub>-CH(OH)-CH<sub>2</sub>-OR" (in which R" represents a C<sub>1-6</sub> alkyl group which may have a substituent, an alkenyl group which may have a substituent or an aryl group which may have a substituent), R<sup>8</sup> and R<sup>9</sup> each independently represents a C<sub>1-6</sub> alkyl group which may have a substituent, an alkenyl group which may have a substituent or an aryl group which may have a substituent, or R<sup>8</sup> and R<sup>9</sup> form, when taken together with the adjacent nitrogen atom, m a nitrogen-containing heterocycle, X<sup>-</sup> represents an anion, and rings C, E, F, G, H and I may each independently have a further substituent or may be cyclocondensed with another aromatic ring),

D represents a nitrogen atom or a group CR" (in which R" represents a hydrogen atom or a C<sub>1-6</sub> alkyl group which may have a substituent), and

B represents the residue of a phenol, aniline, acylacetoarylamide, pyridone, quinoline, isoquinoline, pyrazole, indole, diphenylamine, aminopyridine, pyrimidine, pyrimidone, naphthol, naphthylamine, aminothiazole, thiophene or hydroxypyridine type coupling component.

2. A hair dye composition according to claim 1, further comprising an oxidizing agent.
3. A hair dye composition according to claim 1 or 2, further comprising an oxidation dye.
4. A method for dyeing the hair with a hair dye composition as claimed in any one of claims 1 to 3.



(12)

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Patent- und Rechtsanwälte

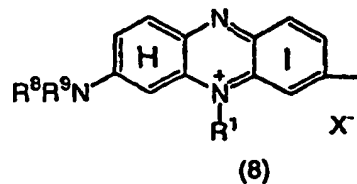
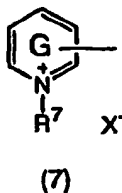
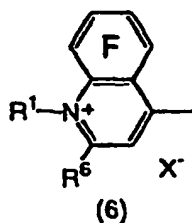
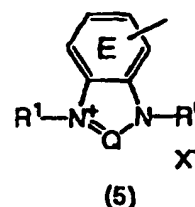
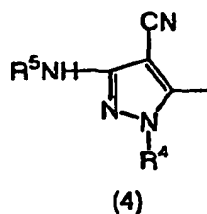
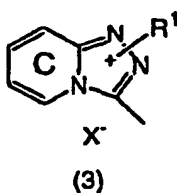
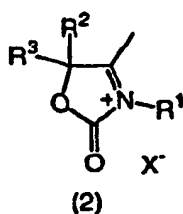
Arabellastrasse 4

81925 München (DE)

## (54) Hair dye composition

(57) Provided is a hair dye composition containing a direct dye A-D=D-B. This hair dye composition has markedly high hair dyeing power, has less color fade over time and undergoes a small change in the color tone of the dye even after storage.

A represents any one of the following groups (2) to (8):



(in which R<sup>1</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup> each represents H, (substituted) C<sub>1-6</sub> alkyl group, etc., R<sup>2</sup> and R<sup>3</sup> each represents (substituted) C<sub>1-6</sub> alkyl group, etc. or form, when taken together with the adjacent C, a cycloalkane ring, Q represents N or group CR', R<sup>7</sup> represents (substituted) aralkyl group or a group CH<sub>2</sub>-CH(OH)-CH<sub>2</sub>-OR'', R<sup>8</sup> and R<sup>9</sup> each represents

H, (substituted) C<sub>1-6</sub> alkyl, etc., or form, when taken together with the adjacent N, a heterocycle, X<sup>-</sup> represents an anion, and rings C-I may each have a further substituent or a condensed ring), D represents N or group CR<sup>m</sup>, and B represents the residue of a coupling component.



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
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X,D	GB 2 054 630 A (ICI LTD) 18 February 1981 (1981-02-18) * formula (3): example, claim 9 * ---	1	
X,D	EP 0 659 839 A (BAYER AG) 28 June 1995 (1995-06-28) * formula (4): example 38, claim 8 * ---	1,4	
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E	EP 1 133 978 A (KAO CORP) 19 September 2001 (2001-09-19) * claims 1-3,6; formula (6): compound (j), examples 16,18,19; formula (7): compound (h), example 24 * --- -/-	1-4	
The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 13 November 2003	Examiner Werner, S
<b>CATEGORY OF CITED DOCUMENTS</b> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

EPO FORM 1503 03.82 (P04C01)



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (In I.C.I.7)
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The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 13 November 2003	Examiner Werner, S
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons &amp; : member of the same patent family, corresponding document</p>			

EPO FORM 1503 03.02 (P04C01)





### CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing more than ten claims.

- ☐ Only part of the claims have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims and for those claims for which claims fees have been paid, namely claim(s):
- ☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims.

### LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

see sheet B

- ☒ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.
- ☐ As all searchable claims could be searched without effort justifying an additional fee, the Search Division did not invite payment of any additional fee.
- ☐ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims:
- ☐ None of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims:



The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

1. Claims: 1-4 in part

hair dye composition comprising a compound according to formula (1) in combination with formula (2) and associated method of dyeing hair

2. Claims: 1-4 in part

hair dye composition comprising a compound according to formula (1) in combination with formula (3) and associated method of dyeing hair

3. Claims: 1-4 in part

hair dye composition comprising a compound according to formula (1) in combination with formula (4) and associated method of dyeing hair

4. Claims: 1-4 in part

hair dye composition comprising a compound according to formula (1) in combination with formula (5) and associated method of dyeing hair

5. Claims: 1-4 in part

hair dye composition comprising a compound according to formula (1) in combination with formula (6) or formula (7) and associated method of dyeing hair

6. Claims: 1-4 in part

hair dye composition comprising a compound according to formula (1) in combination with formula (8) and associated method of dyeing hair

**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

EP 01 11 4801

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.  
The members are as contained in the European Patent Office EDP file on  
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13-11-2003

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

EP 01 11 4801

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.  
The members are as contained in the European Patent Office EDP file on  
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